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(54) Title: STRENGTHENED GRAPHITE SHEET MATERIAL

(57) Abstract

A strengthened exfoliated graphite sheet material and a method for making same is described. The method comprises the steps of applying at least one coat of a liquid plastics material to at least one face of said exfoliated graphite sheet material and drying said at least one liquid coat to leave an adherent plastics material sheet on said graphite sheet material.

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STRENGTHENED GRAPHITE SHEET MATERIAL

The present invention relates to graphite sheet material having improved strength and handlability.

Exfoliated or expanded graphite may be compressed to form sheet material which finds many applications in sealing gaskets for example owing to its high compressibility and conformability. However, exfoliated graphite sheet is relatively very brittle, easily fracturing when bent or roughly handled. Various exfoliated graphite sheet materials having improved strength and durability have been proposed. GB2154675 of common ownership herewith describes an expanded graphite web material having a reinforcing core of thin metal, the material being made by laminating a sheet of expanded graphite to each face of a thin metal, e.g. nickel, sheet by adhesive means. The tensile strength of the resulting graphite sheet is greatly increased. Another proposal has involved the bonding by adhesive means of a plastics material sheet film to one or both faces of a graphite sheet.

Whilst these earlier proposals have resulted in exfoliated graphite sheet having greatly improved strength and durability, they suffer from the disadvantage of being costly to manufacture due, inter alia, to the requirement of needing expensive capital equipment for their production. Furthermore, when a plastics sheet is bonded to graphite sheet the sheet must be at a minimum thickness to enable the sheet to be passed through rollers and applied to the graphite. Thus when the gasket is clamped between two flanges and subject to heat, as in a cylinder head gasket, the plastics will stick to the flange. This

results in the flange having to be cleaned when the gasket has to be replaced. This is costly and time consuming.

It is an object of the present invention to provide exfoliated graphite sheet having greatly improved strength and resistance to handling damage compared to ordinary exfoliated graphite sheet, at an economic cost and to provide a method for its production.

According to a first aspect of the present invention, there is provided strengthened exfoliated graphite sheet material, said exfoliated graphite sheet material having on at least one face thereof a sheet of a plastics material applied initially as a liquid.

According to a second aspect of the present invention, there is provided a method of strengthening exfoliated graphite sheet material, the method comprising the steps of applying at least one coat of a liquid plastics material to at least one face of said exfoliated graphite sheet material and drying said at least one liquid coat to leave an adherent plastics material sheet on said sheet material.

The term "plastics material" used herein is intended to include any suitable polymer and/or synthetic resin or mixture thereof capable of being applied to the graphite sheet in liquid form. The liquid form ma be in the form of a monomer, in melt form or in solution in a solvent for example.

The plastics material sheet may be applied by any suitable method including spraying, brushing, dipping and by electrophoretic methods for example.

The plastics material sheet may be applied in several coats to one or both faces of the graphite sheet material as desired. When more than one coat is applied, each coat may be dried prior to application of the next or alternatively, more than one coat may be dried at a time so long as the total coating is self supporting without running off the sheet surface for example. The number of coats applied will be dependent upon the final desired thickness and strength of the plastics material sheet and the desired degree of enhancement of strength of the graphite sheet.

Depending upon the plastics material being applied, it may also be necessary to further include a curing step in addition to or as part of the drying step. The curing step ma be to polymerise the dried coating and increase the strength of the plastics material coating itself. The temperature at which drying and/or the curing steps will be carried out will be dependent upon the type of plastics material in question.

Where more than one coat of plastics material is applied these may not necessarily all be of the same material.

The thickness of each individual plastics material layer may be controlled to an extent by the viscosity of the applied liquid coat, the greater the viscosity, the thicker each coat may be.

An example of a suitable plastics material may be a water based acrylic polymer resin.

Two or more coats of plastics material may be applied. It has been found that depending upon the

density of the graphite sheet and physical and chemical characteristics of the applied liquid, the first coat tends to penetrate the graphite structure and act as a sealant, whereas a second coat tends to remain substantially completely on the surface due to the sealing effect of the first coat. The strengthening effect of the second coat and any further coats are, therefore, further enhanced. However, it is possible by control of liquid viscosity to minimise penetration of the graphite structure so as to allow the use of a single coat only. Other techniques to prevent penetration such as the addition of fillers to the liquid or the use of anti-wetting agents may also be employed.

However, it may be desirable to achieve penetration of the graphite with a sealing coating so as to improve adhesion of a second coat to the first coat and also to the graphite itself by virtue of deeper penetration of the graphite porosity. Control of the depth of penetration may be controlled inter alia by viscosity of the first coating.

Where the graphite sheet is to be used for gasket applications, it may be further treated so as to provide gasket release properties, i.e. easy removal from surfaces which have been sealed. This may be achieved either by additional surface coating on top of the plastics material coating or by addition of suitable agents to the liquid plastics coating material. In the former case additional surface coatings may comprise polytetrafluoroethylene (PTFE), silicones for example. In the latter case, diluents or agents such as silicones, matting agents, fillers such as silica or ground up minerals such as china clay, and, antioxidants for example may be used. The plastics to filler ratio may be, by volume, less than or

equal to 10:1 or less than or equal to 5:1 or in the region of 4:1.

Strengthened exfoliated graphite sheet according to the present invention is suitable for the manufacture of so-called spiral wound gaskets and also for the protection of already formed spiral wound gaskets by coating thereof. The plastics material coating prevents the edges of exfoliated graphite sheet material from being friable and easily chipping, either during cutting or during subsequent handling and storage.

The surface of the graphite material itself may be treated for example by indenting or shallow spiking or by chemical means so as to improve the mechanical bonding of the resulting plastics material to the surface.

In order that the present invention may be more fully understood, examples will now be described by way of illustration only.

Exfoliated graphite sheet of thickness about 1mm was selected for testing. This material would fracture across its width when bent through a relatively small angle of about 10 to 20°.

Three different self-crosslinking acrylic resin emulsions were chosen for their differing physical characteristics. These were :

Revacryl 274 (trade name) - soft, flexible Tg -24°C
Revacryl 275 (trade name) - tough, flexible Tg -5°C
Revacryl 277 (trade name) - tough, stiff Tg +10°C

Each emulsion was coated by spraying on to the graphite sheet in 1 and 2 coats and bend tests carried out as specified below :

	Bend Test
Revacryl 274, 1 coat	40°
Revacryl 274, 2 coats	90°
Revacryl 275, 2 coats	90°
Revacryl 277, 2 coats	90°**

** This coating material was superior to the others and enabled the graphite sheet to be repeatedly bent through 180° without fracturing.

The samples coated with Revacryl 277 were also completely tack-free at room temperature and the coated graphite material easily cut with scissors without chipping of the edge.

Revacryl 277 may include plastics such as PTFE, china clay in powder form, water and a dispersing agent such as Dispex N40. The ratio of plastics to china clay by volume may be less than or equal to 10:1 or 5:1 and is preferably in the region of 4:1. Such substance may be difficult or impossible to make as a sheet standing by itself and being able to be handled. However, when on the graphite, the sheet has sufficient strength to allow the graphite to be bent. Furthermore, the Revacryl 277 does not tend to stick to flanges and in any event this sheet has less plastics per unit area than a layer that is applied in the form of a sheet thus allowing easy replacement of gaskets.

The reader's attention is directed to all papers and documents which are filed concurrently with or previous to this specification in connection with this application and which are open to public inspection with this

specification, and the contents of all such papers and documents are incorporated herein by reference.

All of the features disclosed in this specification (including any accompanying claims, abstract and drawings), and/or all of the steps of any method or process so disclosed, may be combined in any combination, except combinations where at least some of such features and/or steps are mutually exclusive.

Each feature disclosed in this specification (including any accompanying claims, abstract and drawings), may be replaced by alternative features serving the same, equivalent or similar purpose, unless expressly stated otherwise. Thus, unless expressly stated otherwise, each feature disclosed is one example only of a generic series of equivalent or similar features.

The invention is not restricted to the details of the foregoing embodiment(s). The invention extends to any novel one, or any novel combination, of the features disclosed in this specification (including any accompanying claims, abstract and drawings), or to any novel one, or any novel combination, of the steps of any method or process so disclosed.

CLAIMS

1. A method of strengthening exfoliated graphite sheet material, the method comprising the steps of applying at least one coat of a liquid plastics material to at least one face of said exfoliated graphite sheet material and drying said at least one liquid coat to leave an adherent plastics material sheet on said sheet material.

2. A method according to Claim 1 wherein the plastics material sheet is applied by a technique selected from the group comprising spraying, brushing, dipping and by electrophoretic methods.

3. A method according to either Claim 1 or Claim 2 further including a curing step for the plastics material.

4. A method according to Claim 3 wherein the curing step is included as part of the drying step.

5. A method according to any one preceding claim from 1 to 4, wherein if more than one sheet of plastics material is applied these are not all of the same material.

6. A method according to any one of preceding claims 1 to 5 and further including the step of including a release agent.

7. A method according to claim 6, wherein said release agent is included in said liquid plastics material.

8. A method as claimed in any preceding claim in which the liquid penetrates the graphite.

9. A method as claimed in any preceding claim comprising adding filler to the liquid prior to applying the coat of plastics material.

10. A method of making a strengthened graphite sheet material substantially as hereinbefore described with reference to the accompanying description and examples.

11. Strengthened exfoliated graphite sheet material, said exfoliated graphite sheet material having on at least one face thereof a sheet of a plastics material applied initially as a liquid.

12. A strengthened graphite sheet material according to claim 11 wherein said plastics material is a water-based acrylic polymer resin.

13. A strengthened graphite sheet material according to either claim 11 or claim 12 further including a release agent.

14. A strengthened graphite sheet material according to claim 13 wherein said release agent is provided as a separate outer layer.

15. A strengthen graphite sheet material according to claim 13 wherein said release agent is incorporated into said plastics material sheet.

16, A strengt6hene graphite sheet material according to claim 1 or any one of claims 11 to 15 wherein porosity adjacent the surface of the graphite material is impregnated with the plastics material.

17. A strengthened graphite sheet material according to any of claims 11 to 16 in which the plastics includes a filler.

18. A strengthened graphite sheet material according to claim 17 in which the ratio by volume of plastics to filler is less than or equal to 10:1 or less than or equal to 5:1 or in the region of 4:1.

19. A strengthened graphite sheet material as claimed in any of claims 11 to 18 in which the sheet material is in the form of a spiral.

20. A strengthened graphite sheet material substantially as hereinbefore described with reference to the accompanying description and examples.

A New Approach to Polymer Nanocomposites with Supercritical CO2 Exfoliated Clays

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Abstract:

According to many recently published works, the dispersion of nanolayers of mineral clay was found to boost the thermal stability, mechanical strength, and flame retardancy of polymers. The objective of this research is directed to the delamination of organically modified clays before formation of a polymeric nanocomposite. Supercritical CO2 was chosen as a processing aid to delaminate the layered platelets of organically modified montmorillonite clay. Examination of the supercritical fluid treated clay by Wide-Angle X-Ray Diffraction (WAXD) confirms that the treatment was effective in exfoliation of clay layers. Pressure, temperature and processing time have strong effects on the final structure of clays. Increasing basal spacing (001) or collapsing layered structures were observed. CO2-soluble additives, such as low molecular weight PDMS, were used to coat the delaminated clay surfaces during supercritical process treatment and thus prevent the collapse of the layered structures after depressurization of carbon dioxide.